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Electronic and structural properties of MgS, CaS, SrS and BaS

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Abstract The electronic and structural properties of MgS CaS, SrS and BaS rocksalt structure are studied with the first principle full potential Linearized Augmented Plane Wave (FP-LAPW) method The exchange correlation potential was calculated within the Generalized Gradient Approximation (GGA) using Perdew-Burke-Einzerhof (PBE-GGA) scheme The scalar relativistic approach was adopted for the valence states, whereas the core states are treated fully relativistically Energy band structures density of states and structural parameters of both compounds are presented and discussed in context with the available theoretical and experimental studies Our results are good and show reasonable agreement with previous results even though sufficient experimental values are not available for more realistic comparison

Keywords Full-Potential Linearized Augmented Plane Wave (FP-LAPW) Density Functional Theory (DFT), Local Density Approximation (LDA), Generalized Gradient Approximation (GGA)

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1 Introduction

The monosulphide of Mg, Ca, Sr and Ba crystallize in the rocksalt NaCl (B1) structure and are very exciting materials due to their great technological importance which range from catalysis to microelectronics They have been proposed as good candidates in the areas of multicolor thin-film electroluminscent and magneto optical devices [1]. However, monosulphides are used in X-ray, cathode and photoluminophors, with a bright glow, a great capacity and a bright IR radiation [1-3] In addition, these monosulphides are widely utilized in optics, optoelectronics, television engineering, *etc* Therefore due to the vast technological relevance of these monosulphides, they are widely investigated both theoretically and experimentally [4-12] Despite the works previously done in this area, it has not been possible to fully explain the physical properties of these monosulphides without proper understanding of their electronic structure

In order to understand the behaviour of these monosulphides, the electronic band structure of CaS, SrS and BaS was calculated by Linear Augmented Plane Waves (LAPW) [7] The Tight-Binding Linear Muffin-Tin Orbital (TB-LMTO) method was utilized in description of the electronic band structure of MgS and MgSe and the density of state of the sulphides [13] Later, the electronic structure of the oxides and sulphides of Mg, Ca, Sr was computed with the use of self-consistent Hartree-Fock method including correlation [14] Also the self-consistent Orthogonalised Linear Combination of Atomic Orbitals (OLCAO) method in the local density approximation (LDA) was used in the calculation of the band structure of alkali earth metals of sulphides [15] Few years ago, schematic band structure models were used for MgS, CaS and MnS [16] Recently, the Full-Potential Linear Muffin-Tin Orbitals (FP-LMTO) method augmented by a Plane Wave (PLW) basis, was utilized in the study of structural and electronic properties of MgS and MgSe [17] Drief and coworkers [18], carried out first principle calculation of structural, electronic, elastic and optical properties of MgS, MgSe and MgTe in the framework of density functional theory within the local density approximation using the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method Also, projected density of states in the conduction band of CaS and MgS was used in the electronic structure

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calculation [8]. Even though many workers had in the past used Density Functional Theory (DFT) in the calculation of the electronic structure of these monosulphides, it is still necessary to employ a first principle approach in order to display some features of the electronic and structural properties of these materials.

Therefore, the present study will adopt the first principle Full Potential Linearized Augmented Plane Wave (FP-LAPW) method [19] using the Density Functional Theory (DFT) in its Local Density Approximation (LDA). In this approach, the exchange and correlation potential is incorporated in the Generalized Gradient Approximation (GGA) using the scheme of Perdew-Burke-Ernzerhof (PBE-GGA) [20]. This paper is arranged as follows: Section 2 will briefly describe the computational technique adopted in the calculation of the electronic properties of MgS, CaS, SrS and BaS. In Section 3, the results obtained will be used to compare with the previous theoretical and experimental studies. The conclusion of this work will be drawn in Section 4.

2. Method of calculation

In this section, we present the computational technique in the study of the electronic properties of monosulphides MgS, CaS, SrS and BaS which crystallize in the rocksalt structure. Here, we used the Full Potential-Linearized Augmented Plane Wave (FP-LAPW) method within the Density Functional Theory in its Local Density Approximation. The calculation is done with WIEN 97 package developed by Blaha *et al* [21]. In this package, a basis set is obtained by dividing the unit cell into non-overlapping atomic spheres and an interstitial region. Within the atomic sphere, we used a linear combination of radial functions multiplied by spherical harmonics, whereas within the interstitial region, we used a plane wave expansion which is augmented by an atomic-like function in every atomic sphere. In this calculation, the exchange and correlation potential is incorporated by using the scheme of Ceperly-Alder as was parameterized by Perdew-Zunger [22] and in GGA, by using the scheme of Perdew-Burke-Ernzerhof (PBE-GGA) [20].

In the present calculation, therefore, the sphere radii of Mg, Ca, Sr and Ba are chosen as 2.3, 2.8, 2.7 and 2.8 atomic units respectively, whereas the sphere radii for the corresponding S are 2.4 atomic units. In these spheres, the charge density and potential are expanded in terms of crystal harmonics up to angular momenta l = 6. We carried out the Brillouin zone integration by using 100 K-points in the irreducible Brillouin zone. The convergence was obtained at $R_{MT}K_{max} = 9$, where R_{MT} is the atomic sphere radii and K_{max} is the interstitial plane wave cut-off.

3. Results and discussion

In this work, the structural parameters of MgS, CaS, SrS and BaS were obtained by calculating the total energy at various values of the lattice parameters around the experimental values. This was carried out within the FP-LAPW method with GGA scheme without the spin orbit coupling effects. By fitting the Murnaghan equation of state [23] to total energies *versus* lattice parameters, we obtained the equilibrium lattice parament (a_{eq}), bulk modulus B and pressure derivative of bulk modulus B' which are compared with previous theoretical and experimental studies in Table 1. Here, present results for MgS, CaS, SrS and BaS are compared with previous experimental and theoretical results. The band structures of MgS, CaS, SrS and BaS in rocksalt structure are shown in figures 1, 2, 3 and 4 respectively while the density of states for MgS, CaS, SrS, and BaS are shown in

Table 1. Structural parameters of MgS, CaS, SrS and BaS.

	Present work	Other calculated values					Experiment
MgS							
a(Å)	5.2402	5.142[25]	5.203[15]	5.135[26]	5.244[17]	5.16[13]	5.2033[24]
B(Mbar)	0.742	0.828[25]	0.777[26]	0.851[17]	0.819[13]		
B'	4.2702	3.98[26]	3.5[26]	3.077[17]	4.03[13]		
CaS							
a(Å)	5.7242	5.69[15]	3.8[8]	1.75[6]			5.690[24]
B(Mbar)	0.569						
B'	4.1778						
SrS							
a(Å)	6.0658	6.076[30]	5.774[34]				6.02[33]
B(Mbar)	0.469	0.47 [30]	0.62 [34]				0.58[33]
B'	5.1306	4.19 [30]					
BaS							
a(Å)	6.4312	6.294[35]					6.387[27]
B(Mbar)	0.448	0.524[35]					0.394[27]
B'	5.3099						

Table 2. Energy band gaps (eV) for MgS, CaS, SrS and BaS

	Present Work	FP-LMTO	LDA	Other Calculated values			
MgS	2.794	2.76	2.657	2.7[14]	2.7[13]	4.59[15]	4.6[8]
CaS	2.4			3.2[15]	3.5[8]	2.13[7]	
SrS	2.488			2.3[31]	2.45[30]		
BaS	2.2097			2.3[28]	2.1[29]		

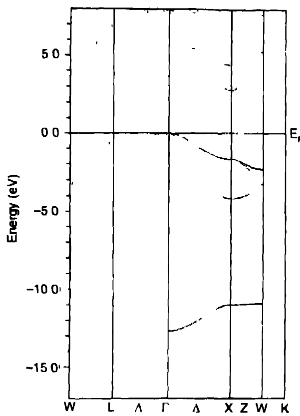

Figure 1. Band structure of MgS

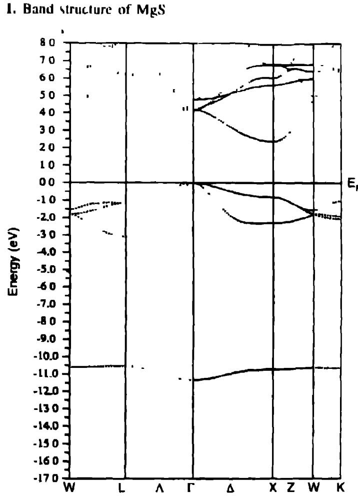

Figure 2. Band structure of CaS

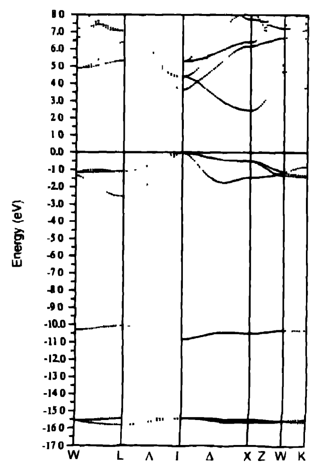

Figure 3. Band structure of SrS

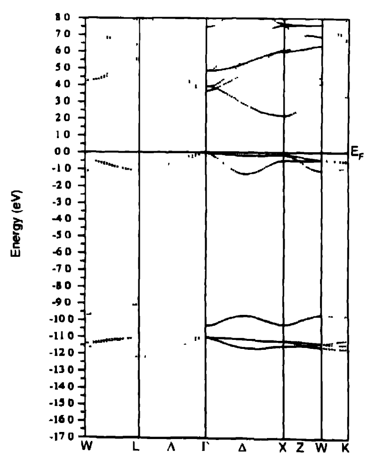

Figure 4. Band structure of BaS

figures 5, 6, 7 and 8. In MgS, valence band maximum occurs at the Γ point. This observation is in agreement with earlier works using the Tight Binding Linear Muffin-Tin Orbital method [13] as well as in the self-consistent Hatree-Fock method including correlation [14]. Similarly, for the CaS, SrS and BaS, the valence band maximum occurs at the G point. Thus, all four compounds, MgS, CaS, SrS, and BaS, are found to be indirect band gap materials with the band gap occurring between G and X point This result is in agreement with earlier calculation by the LAPW

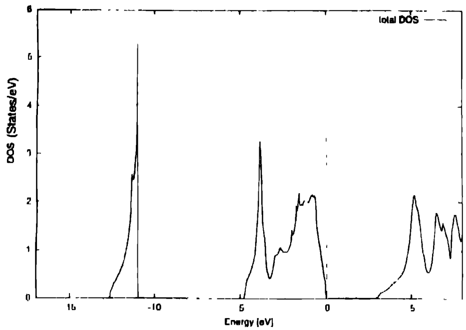

Figure 5. Total density of states of MgS

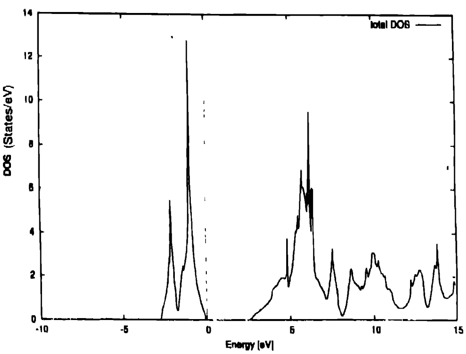

Figure 6. Total density of states of CaS

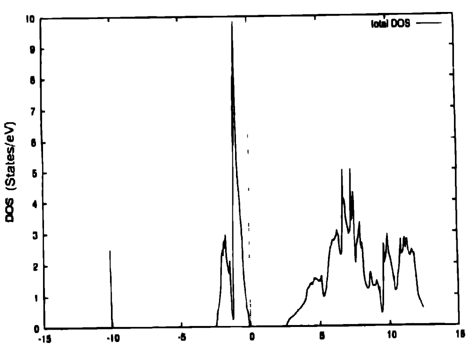

Figure 7. Total density of states of SrS

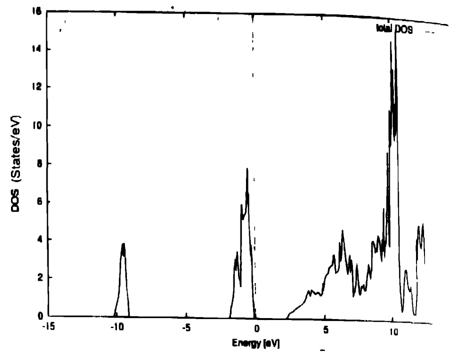

Figure 8 Total density of states of BaS

method [7] The energy band gaps obtained from MgS, CaS, SrS, and BaS are given in Table 2 The values are compared with previous studies It is seen that our results agree favourably with past results

3. Conclusions

In this paper, we have used the first principle Full Potential Linearized Augmented Plane Wave (FP-LAPW) method using the Density Functional Theory (DFT) in its Local Density Approximation (LDA). The exchange and correlation potential within the LDA is calculated by adopting the scheme of Ceperley – Alder as parameterized by Perdew – Zunger and within the Generalized Gradient Approximation (GGA) using the scheme of Perdew – Burke – Einzerhof (PBE – GGA) The scalar relativistic approach was adopted for the valence state while the core states are treated fully relativistically In this way we have calculated the equilibrium lattice parameter (a_0) bulk modulus B, pressure derivative of bulk modulus B' and energy band gaps for MgS, CaS, SrS and BaS The results obtained show that MgS, CaS, SrS and BaS are indirect band gap materials. In this work, our results are comparable with the values obtained with other techniques even though enough experimental values are not available for more realistic comparison

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